The Dipolar and Conductivity Relaxations of Epoxy Coating Studied by EIS in Aqueous Solution

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Introduction

The organic polymer coatings are largely used to protect metallic structures from the corrosion in aqueous medium, but the absorption of water (water-uptake) induces the degradation of these protective layers. An equivalent circuit model describing the electrochemical behavior of paint coated electrode involving flaw areas was proposed in our earlier work [1].

However, as shown in a previous paper, this model cannot represent EIS of flawless film and the permittivity relaxation of polymer layer itself, influenced by absorbed water in polymer layer, becomes the major phenomenon [2]. The presence of this dielectric layer is observed as a capacitance $C(\omega)$ in EIS. $C(\omega)$ is linked to the permittivity through a plane condenser model:

$$C(\omega) = \varepsilon(\omega)\, \varepsilon_0\, S / d \qquad (1)$$

ε_0, S, and d stand respectively for the dielectric constant of vacuum, the surface area, and the thickness of dielectric material. $\varepsilon(\omega)$ *may* follow the Havriliak-Negami's relationship including the conductance through a polymer film [2]:

$$\varepsilon(\omega) = \varepsilon(\infty) + \Delta\varepsilon / \{[1+(j\, \omega\, \tau)^{\alpha}]^{\beta}\} + \kappa / [\varepsilon_0\ (j\, \omega)^{\gamma}]$$
$$\text{with } \Delta\varepsilon = \varepsilon(0) - \varepsilon(\infty) \qquad (2)$$

Where ω, τ, $\Delta\varepsilon$, $\varepsilon(\infty)$ and $\varepsilon(0)$ denote respectively the angular frequency, the dipolar relaxation time-constant, the dispersion strength of dipolar relaxation, and the high and low frequency limits of permittivity. α *and* β are empirical constants to describe the frequency dispersion. κ and γ are the conductivity of polymer film and an empirical constant accounting for the frequency dependence of ionic conduction.

From experimental EIS results, so called Cole-Cole capacitance $C_c(\omega)$ was calculated:

$$C_c(\omega) = 1/[j\, \omega\, (Z(\omega) - R_{\Omega})] \qquad (3)$$

R_{Ω} stands for the solution resistance. This capacitance can be expressed by the sum of dielectric relaxation $C_{\varepsilon}(\omega)$ and ionic resistance of film that depends ω:

$$C_c(\omega) = C_{\varepsilon}(\omega) + 1/ [R_f\, (j\, \omega)^{\gamma}] \qquad (4)$$

By combining Eqs 1 to 3, one gets readily

$$R_f = \varepsilon_0\, d / \kappa S \qquad (5)$$

The fractional volume of water ϕ absorbed by polymer layer is expected to follow Fick's law [4] hence $\varepsilon(\omega)$, however, abnormal sorption kinetics will be observed when the relaxation of macromolecular-chains is slower than diffusion process. Then no capacitance plateau corresponding to the water saturation will be detected.

Results and Discussion

Figure 1 presents the Cole-Cole capacitance. This result is in agreement with that predicted by Eq 4. The values of parameters defined in Eq 2 were calculated by a simplex regression method. Among others, it was found that: R_f=20 GΩ cm^2, γ=0.859, $\varepsilon(\infty)$=5.4, and $\varepsilon(0)$=8.88. R_f

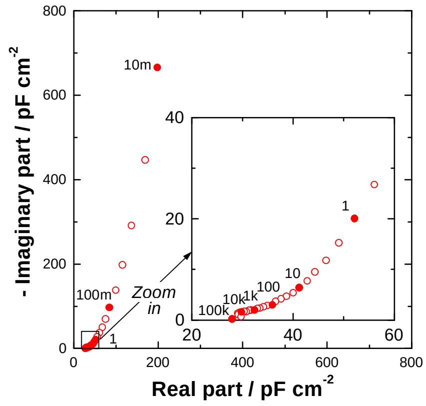

Figure 1: Cole-Cole plot of experimental EIS data. Mild steel coated by 180µm epoxy paint in an artificial irrigation water. After 80min of immersion.

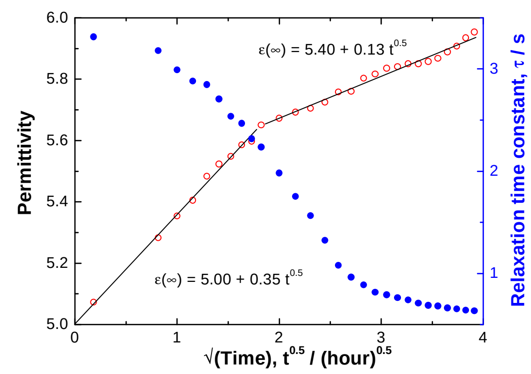

Figure 2: Effect of water-uptake to ε(∞) and T.

value corresponds approximately to the chord of capacitance loop observed by impedance diagram.

Figure 2 presents $\varepsilon(\infty)$ and τ changes vs. the square root of immersion time. τ decreased with time indicating a plasticizing effect of absorbed water. But both $\varepsilon(\infty)$ and τ showed an inflexion point at *ca*. 4 hours. Therefore, abnormal sorption kinetics was introduced to interpret these experimental data. The comparison with the results obtained with epoxy-vinyl coating will be done.

Conclusion

EIS technique was applied to study the water uptake of an epoxy coating. The Cole-Cole capacitance spectra calculated from impedance data were interpreted in terms of macromolecular mobility leading to the dipole relaxation. The water uptake was characterized by the $\varepsilon(\infty)$ increase, and a plasticizing effect of this absorbed water by the decrease of relaxation time constant. It was also remarked that an abnormal sorption kinetics is taking place.

References

1. L. Beaunier, I. Epelboin, J.C. Lestrade, H. Takenouti; *Surface Technology*, **4**, 237 (1976).
2. S. Duval, Y. Camberlin, M. Glotin, M. Keddam, F. Ropital, H. Takenouti; *Progress in Organic Coatings*, **39**, 15 (2000).
3. A.K. Jonscher; "*Dielectric relaxation in solids*", Chelsea Dielectric Press, London, (1983).
4. J. Crank; "*The mathematics of diffusion*" 2nd edition, Oxford Scientific Publications (1975).